COMPLETE SPECIFICATION

Improved Process of Hydroisomerization of Hydrocarbons

We, GULF RESEARCH & DEVELOPMENT COMPANY, a corporation organized under the laws of the State of Delaware, United States of America, of Gulf Building, Pittsburgh, Pennsylvania, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a catalytic hydroisomerization process for the treatment of hydrocarbons to convert them to more valuable products. More particularly, the invention relates to a process for the catalytic hydroisomerization of hydrocarbons of the naphtha or gasoline boiling range to increase the value of such hydrocarbons as components of fuels for internal combustion engines.

The process of the invention can be employed for the isomerization of a single straight chain or slightly branched chain paraffin or a mixture of such paraffins and also to the isomerization of a single naphthene or a mixture of naphthenes. It can also be employed for the conversion of natural or casinghead gasolines, which are usually largely paraffinic in composition, and for the conversion of straight run petroleum naphthas. Naphtha or gasoline fractions which contain a relatively large proportion of paraffins, for example 50 per cent or more, are especially valuable charge stocks for the present process. However, the advantages of the invention are obtained at least to some extent when charging other naphthas. Regardless of the charge stock to the process, the process is characterized in that high yields of good quality products are obtained.

As will appear from the following description, when a naphtha fraction is employed as the charge stock, the present process is related to hydroforming. In hydroforming, however, the principal objective has been to promote reactions yielding aromatics, such as the dehydrogenation of naphthenes and the dehydrocyclization of paraffins, at the expense of iso-

merization reactions and with necessary concomitant cracking of components of the charge stock, particularly the paraffinic constituents. In the present process, conditions are maintained, including high temperatures, which are conducive to the isomerization of paraffins and naphthenes while avoiding excessive cracking and dehydrogenation of the charge stock. Thus, while dehydrogenation reactions take place in the present process, the dehydrogenation of a naphthene constituent of the charge, such as methyl cyclopentane, will occur after substantial isomerization has taken place. As a result, a substantial proportion of methyl cyclopentane is converted to benzene. Simple dehydrogenation reactions take place principally with respect to the six carbon atom naphthene ring compounds, yielding hydrocarbons of the benzene series.

The process of the invention comprises contacting the hydrocarbon and hydrogen in proportions of at least 500 cubic feet of hydrogen per barrel of said hydrocarbon with a catalyst comprising a molybdenum oxide at a pressure above 50 pounds per square inch and at a temperature of at least 850° F. and including in the charge to the reaction zone an amount of oxygen, steam or carbon dioxide supplying 0.0023 to 0.03 mol of oxygen per mol of hydrogen. The hydrogen separated from the product will usually be recycled to the reaction zone with or without make-up hydrogen. The reaction pressure is preferably about 100 to about 2000 pounds per square inch. (These pressures are gauge pressures as are other pressures mentioned in the specification and claims). The effects of hydrogen concentration and reaction pressure are related and it is preferred to use higher pressures when employing the lower hydrogen concentrations.

We have discovered in accordance with the invention that by introducing the oxygenic substance as aforesaid (oxygen, steam or carbon dioxide) into the reaction zone with the charge stock and hydrogen, the nature of the reactions taking place is altered so that the

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extent of isomerization is substantially increased while dehydrogenation and cracking of paraffins are decreased as compared with the relative extent of these reactions taking place under the same conditions but without the addition of such oxygenic substance. We have also discovered that in operations designed to produce a selected yield of liquid product, the temperature in the present process should be maintained at least 50° F. above the temperature at which an equal amount of liquid product would be obtained when subjecting the charge stock to identical reaction conditions but omitting the use of the oxygenic substance as aforesaid.

While the molybdenum oxide can be used alone, it is preferably used in combination with a carrier such as activated alumina, alumina gel, peptized alumina gel, silica gel, silica-alumina gel, aged or deactivated silica-alumina cracking catalysts, silica, magnesia gel, magnesia, titania, bauxite, and the like. A particularly suitable support comprises alumina stabilized with about 5 per cent by weight silica.

The results of our procedure of high temperature hydroisomerization while adding an oxygenic substance as aforesaid to the conversion zone as compared with results of a similar operation in which no oxygenic substance is added include markedly improved conversion to desired products and high desired product yields. The superior results of our procedure are obtained with all of the suitable charge stocks. Thus, the conversion of straight chain paraffins to the branched chain isomers is considerably improved while total liquid yields are substantially as good or improved, and in the treatment of paraffinic naphthas our process in addition to high conversion of straight chain paraffins to branched chain isomers also shows good conversion of naphthenes to aromatic and high liquid yields. It will be understood that in referring to liquid products, we mean butanes and heavier.

While it is not intended to limit the invention to any theory, the research work in connection with the invention has indicated that the inclusion of the oxygenic substance in the aforesaid amount in the total charge to the reaction zone has an effect on the state of oxidation of the molybdenum oxide catalyst so that the catalyst is maintained in a gross sense in a state of oxidation between the highest oxide which the metal is capable of forming and the free metal. For example, this catalyst would ordinarily be used in a reaction cycle comprising a reaction period, a regeneration period and a reduction period. Thus, the molybdenum catalyst as employed at the beginning of the reaction period might be a mixture of the free metal, MoO_2, and possibly a lower oxide. Under conventional hydroforming conditions, presumably the catalyst undergoes no further oxidation but rather additional reduction. By including the aforesaid amount of the oxygenic substance in the charge to the reaction zone in accordance with our invention, it is believed that conditions are created in the reaction zone conducive to the conversion and/or maintenance of at least the surface layer of the molybdenum catalyst substantially in the form of MoO_2. It is frequently desirable to include the aforesaid amount of oxygenic substance in the hydrogen employed for reducing the catalyst prior to the conversion reaction. When this is done, the pre-reduction will proceed only so far as to convert the surface of the catalyst to a state of oxidation corresponding substantially to MoO_2. The use of the oxygenic substance in the charge to a reaction zone containing a catalyst prereduced in this manner will accomplish primarily maintenance of the desired gross state of oxidation of the catalyst. The results obtained in the practice of the invention show that when at least the surface of the catalyst is substantially in the form of MoO_2, the catalyst is particularly effective as a hydroisomerization catalyst at elevated temperatures.

The oxygenic substances, namely, free oxygen, steam, and carbon dioxide, are readily available and produce no complicating side reactions.

We have indicated previously that the reaction temperature for optimum results should be at least 50° F. higher in the present process than in a similar process in which the state of oxidation of the catalyst is not controlled. As indicated above, the molybdenum in a hydroisomerization catalyst following oxidative regeneration which is ordinarily employed after a period of hydrocarbon conversion, exists substantially as molybdenum trioxide. The catalyst in this state is too inactive for optimum isomerization but when placed on stream and contacted with the charge of hydrocarbons and hydrogen, the catalyst is reduced to molybdenum dioxide and to a certain amount of lower oxide and/or free molybdenum having excessive cracking activity. Also, when the regenerated catalyst is reduced prior to contacting it with charge, it also reaches a stage of reduction characteristic of excessive cracking activity. Conversion at elevated temperatures with the catalyst in this state results in low liquid product yields. We have discovered that the excessive cracking activity which the molybdenum catalyst develops when contacted with hydrogen can be avoided by introducing as aforesaid the oxygenic substance to the reaction zone during the on-stream period. Thus, while by conventional tests the catalyst appears less active at the same operating conditions, the decrease in over-all activity is largely due to the elimination of hydrocracking activity. Accordingly, where the oxygenic substance is employed in the reaction and

maximum isomerization is desired, the reaction is preferably carried out under reaction conditions including a substantially higher reaction temperature than employed in the absence of the added oxygenic substance.

In many instances the temperature should be substantially higher in our process than 50° F. above the temperature required for the same liquid yield in the absence of the oxygenic substances. Thus, in the hydroisomerization of normal pentane with the introduction of oxygen to the conversion zone in accordance with our procedure, the temperature is preferably at least about 200° F. higher than the temperature required for best results in hydroisomerizing normal pentane without adding oxygen. This is surprising inasmuch as the hydroisomerization of normal pentane in the absence of added oxygenic substances at a temperature 200° F. above the optimum temperature for such hydroisomerization would result in substantially complete gasification of the charge. The operable temperature range for our process in general is between 850° and 1100° F., with the temperatures at the lower end of the range being suitable for the heaviest stocks to which our process is applicable.

The hydrogen concentration in the present process is maintained at 500 to about 30,000 cubic feet of hydrogen per barrel (42 U.S. Gallons) of liquid hydrocarbon charge and preferably at about 1,000 to about 20,000 cubic feet per barrel. Initially in the process it may be necessary to supply this hydrogen from an extraneous source, but since the reactions occurring during the reaction period are generally not hydrogen consuming or are hydrogen productive, as the reactions proceed, the hydrogen requirements can usually be met predominantly or entirely by recycle or hydrogen from the product.

The process of the present invention can be carried out according to several alternative methods of operation. For example, the process can be carried out with the catalyst in a stationary fixed bed, in which case the catalyst is usually in the form of granules or pellets. When using the catalyst in a fixed bed in an operation where periodic regeneration is practiced, the reaction cycle, including the on-stream period and the regeneration period, is carried out on the catalyst in the reaction zone.

The process can also be carried out utilizing a finely divided catalyst in a fluidized state. While in this case the on-stream and regeneration operations also can be both carried out with the catalyst in the reaction zone, it is generally preferred to provide a separate regenerator to which catalyst from the reactor can be conveyed continuously or periodically. The regeneration can be accomplished at about the pressure in the reactor or at lower pressures, for example, atmos-

pheric pressure.

The space velocity can be between about 0.25 and 10.0 volumes of hydrocarbon per hour per volume of catalyst (based on packed catalyst volume). Generally a space velocity of about one-half to three vol./vol./hour is preferred.

Where the over-all effect of the reactions taking place is endothermic, provisions are made for supplying heat to the reaction zone during the on-stream period, such as by preheating the hydrocarbons, hydrogen, and catalyst to a suitable temperature.

There are a number of possible methods of introducing the required oxygenic substance to the reaction zone in accordance with our invention. Thus, using oxygen gas as an example, a small quantity of oxygen can be mixed directly with the hydrogen recycle stream prior to its passage through the preheater and before its mixture with the hydrocarbon charge. In this case precautions should be taken to avoid explosion as by mixing a large proportion of an inert gas such as dry gas (methane, ethane, and propane) with the oxygen before adding it to the hydrogen. Another possible procedure is to introduce the oxygen directly into the catalytic reactor. In the case of a fluidized catalytic reactor, the oxygen preferably is introduced at the bottom of the reactor so as to facilitate its contacting the entire catalyst bed. In the case of a stationary fixed bed catalyst, it may be necessary to introduce the oxygen at a number of points so as to achieve uniform treatment of the entire bed. Still another method of introducing at least a part of the required oxygen to the catalytic reactor is to dissolve oxygen in the liquid hydrocarbon charge.

A method of introducing oxygen to the reactor which can be used in moving bed fluidized catalyst processes is the incorporation of oxygen in the aforesaid amounts in the catalyst transporting gas which is used to transport catalyst from the regenerator to the reactor.

We have stated that the catalyst following regeneration can be placed on stream in the hydro-isomerization process either with or without a prereduction. However, in the event that no reduction is employed, starting the reaction with a completely oxidized catalyst will result in an initial period of uneven reaction conditions. There is also a short period of uneven conditions even if the catalyst is prereduced with hydrogen, during which the catalyst assumes its desired equilibrium state of oxygenation. Also, the catalyst prereduced with hydrogen may not reach optimum activity because the oxygenic substance may only retard the further reduction and may not accomplish reoxidation to the desired state of oxidation. A highly satisfactory procedure for eliminating either of these possibilities of an uneven initial reaction period is the reduction

of the catalyst, before its being placed on stream, with a mixture of hydrogen and the oxygenic substance preferably in the proportions used in the on-stream period. In this way the catalyst can be adjusted to its desired equilibrium state of oxidation before being placed on stream, and uniform reaction conditions can be maintained throughout the cycle. This procedure of prereducing the catalyst with a mixture of hydrogen and oxygenic substance is applicable to either the fixed bed or moving bed procedures, whether using stationary or fluidized type catalysts.

A particularly suitable method of maintaining the proper oxidizing conditions in the reaction zone is to recycle the steam formed in the reactor so that addition of fresh oxygenic substances is unnecessary after the initial equilibrium is achieved. The recycle of steam in the proper amount can be accomplished by maintaining the hydrogen to be recycled at a sufficiently high temperature to prevent condensation of the desired concentration of water vapor, and returning the water vapor to the reaction zone with the recycled hydrogen. If a higher content of oxygenic substance is desired, fresh oxygenic substance can be added to the hydrogen recycle stream.

The beneficial effects of the addition of the oxygenic substance to the hydroisomerization reactor on a molybdenum catalyst are obtainable at a very low content of oxygen in the reaction gases. The upper limit corresponds to 0.03 mol of oxygen per mol of hydrogen. Actually in the case of oxygen, it is generally not advisable to add substantially more than about 0.01 mol of oxygen per mol of hydrogen, because in such case the safe composition for a non-explosive mixture of hydrogen and oxygen may be exceeded. The higher concentrations of oxygen in hydrogen are only obtainable by use of steam or CO_2. Steam, which per mol contains only 0.5 mol of molecular oxygen, must be used in double the volume required for pure oxygen. If steam is used as the oxygenic substance, the maximum concentration of the oxygenic substance may be affected by the steam stability of the catalyst which is being used. Generally, a steam partial pressure of about 50 pounds per square inch should not be exceeded so that when the reaction pressure is high the steam stability of the catalyst could govern the maximum concentration of oxygenic substance which could be used.

Sulfur has a detrimental effect on the catalysts in our process and although there is some variation in sulfur tolerance, it can be said in general that the beneficial effects of the addition of oxygen are lost or greatly decreased when the catalyst is substantially sulfided. The molybdenum catalyst drops considerably in activity when the molybdenum is about 50 per cent sulfided, i.e., when the catalyst contains about 50 per cent of the amount of sulfur required to convert the molybdenum to molybdenum disulfide, and the benefit of operating with the oxygenic substance in the hydrogen is lost. Consequently, it is desirable to employ charge stocks of low sulfur content in order to operate for long on-stream periods without regeneration. When treating a high sulfur stock such as West Texas naphtha by our process, a prior desulfurization treatment may be required if long throughputs are desired, although it may be more convenient to have no prior desulfurization treatment and instead to regenerate the sulfided catalyst at frequent intervals. When the process uses a catalyst which is damaged by regeneration, the sulfiding should be avoided by the prior desulfurization of charge stocks having high sulfur contents.

We have conducted hydroisomerization runs in accordance with the process of our invention which show the superiority of our process, whether petroleum fractions or other hydrocarbons are used as charge stocks, over processes in which no oxygenic substance is added to the conversion zone. The details of procedure were as follows:

EXAMPLE 1

A molybdena-on-alumina fluid catalyst consisting of 10.8 per cent by weight molybdenum trioxide deposited on activated alumina co-precipitated with about 5 weight per cent silica was calcined in air at 1100° F. for several hours and then reduced in a stream of pure hydrogen at 1050° F. for 4 hours. Then to hydroisomerize a 375° F. end point West Texas straight run naphtha having the inspection data listed in Table I below, the reduced catalyst was brought to reaction conditions including a temperature of 968° F., a pressure of 300 pounds per square inch gauge, a space velocity of 1.0 volume of liquid naphtha per hour per volume of catalyst (based on densely packed catalyst volume), and a hydrogen concentration of about 20,000 standard cubic feet of hydrogen per barrel of naphtha over a throughput of 1.0 volume of naphtha per volume of catalyst. Following this lining-out period, product was collected for an on-stream throughput of 2.0 volumes of naphtha per volume of catalyst. The hydrogen used in the lining-out and on-stream periods contained oxygen in the amount of 0.44 per cent by volume. The results of this run in terms of product yield and characteristics are listed in Table I below.

EXAMPLE 2

The molybdena-alumina fluid catalyst of Example 1 was calcined and nitrogen purged and then reduced in a stream of hydrogen containing 0.34 volume per cent oxygen for 4 hours at 1050° F. The catalyst was then placed on-stream to hydroisomerize the West Texas naphtha in the manner described in Example 1 with the exceptions that the reaction temperature was 924° F. and the

hydrogen charged to the reactor contained 0.34 volume per cent oxygen.

EXAMPLE 3

The procedure of Examples 1 and 2 was repeated using a reaction temperature of 890° F. The hydrogen used in the prereduction and the on-stream period contained 0.25 volume per cent oxygen. The results are recorded in Table I below.

We have also conducted runs in the absence of added oxygen for comparison with the results of our process. The details of procedure were as follows:

EXAMPLE 4

The West Texas naphtha charged in Example 1 was treated in a similar manner with the same catalyst at a temperature of 875° F. but using substantially oxygen-free hydrogen (i.e., containing less than 0.01 volume per cent oxygen) for the prereduction and the on-stream period. No oxygenic substances were introduced to the conversion zone during the process. The results are recorded in Table I below.

EXAMPLE 5

The procedure of Example 4 was repeated using a temperature of 840° F. The results are recorded in Table I below.

TABLE I

Example No.		1	2	3	4	5
Temperature: °F.		968	924	890	875	840
Pressure: psig.		300	300	300	300	300
On-stream throughput: Vol./Vol.		2	2	2	2	2
Space velocity: Vol./Hr./Vol.		1	1	1	1	1
Space velocity: Wt./Hr./Wt.		0.76	0.76	0.76	0.76	0.76
Hydrogen rate: STP Cu. Ft./Bbl.		20,300	19,200	20,100	20,600	19,700
Oxygen, in Hydrogen stream, % by Vol.		0.44	0.34	0.25	<0.01	<0.01
Recovery: % by Wt. of Liquid Charge						
Liquid Product		71.5	78.9	84.1	75.0	83.4
Dry gas		14.9	8.7	6.6	13.1	9.0
Wet gas		7.5	6.7	4.8	5.5	3.7
Carbon		0.3	0.3	0.3	0.3	0.3
Total		94.2	94.6	95.8	93.9	96.4
Recovery: % by Vol. of Liquid Charge						
Liquid product		69.5	77.7	83.4	75.0	83.3
10 RVP product		74.7	84.4	93.5	81.3	93.4
	Charge					
Properties of Liquid Product						
Gravity: °API	50.1	45.1	47.3	48.5	50.2	49.9
Sp. Gr., 60/60°F.	0.7792	0.8012	0.7914	0.7861	0.7788	0.7800
Sulfur, wt. %	0.256	0.012	0.010	0.009	0.014	0.010
Olefins: % by Vol.	1.6	0.9	1.2	1.0	1.6	0.8
Bromine No.	1.9	1.3	1.6	1.3	21.	1.0
Aromatic Content: % by Vol.	13.9	63.1	52.8	45.5	47.9	41.7
Vapor Pressure, Reid: Lb./Sq. in.	0	6.0	5.4	3.7	5.7	3.7
Distillation, Gasoline						
Over point: °F.	270	109	104	120	114	130
End point: °F.	375	417	409	408	386	401
10% at: °F.	297	149	158	188	165	197
50	316	268	282	296	261	286
90	343	336	340	344	328	330
Octane No., Micro Research Method:						
Clear	34.8	97.0	91.5	83.3	87.2	78.8
+3 cc. TEL (tetra-ethyl lead)	52.8	106.1	98.4	94.5	96.8	91.8

TABLE I (continued)

Example No.	1	2	3	4	5
Properties of 10 RVP Product					
Gravity: °API	49.2	51.8	54.5	54.4	55.8
Olefins: % by Vol.	0.8	1.1	0.9	1.5	0.7
Aromatic Content: % by Vol.	58.7	48.6	40.6	44.2	37.2
Octane No., Micro research method:					
Clear	97.2	92.2	85.1	88.2	81.1
+3 cc. TEL (tetra-ethyl lead)	106.3*	99.1	96.3	97.8	94.1
Butanes					
% by Vol. required for 10 RVP**	17.4	6.9	7.9	10.8	7.9 10.8
% by Vol. available**	0	12.9	10.2	6.7	8.8 5.1

* Performance number.
** Based on volume of 10 RVP gasoline.

In the tables the abbreviation RVP means Reid Vapor Pressure, that is, vapor pressure by the method described in booklet D323—52 of the American Society for Testing Materials. Gravity °API is the specific gravity determined by the method of booklet D287—52 of the American Society for Testing Materials.

The "Hydrogen Rate" is determined at standard temperature and pressure.

Table I clearly shows the superior results obtainable by the process of our invention in terms of gasoline yields and octane ratings. An
5 even clearer representation of the improvement is afforded by Figure 1 of the accompanying drawings which plots the data from Table I for liquid product yield and Research Octane . Numbers, clear, of the total liquid
10 product, adjusted to 10 pounds Reid Vapour Pressure by the addition of butanes..

Referring to Figure 1 of the drawing, Curve A plots the data for Examples 1, 2, and 3, and Curve B plots the data for Examples
15 4 and 5. It is clear from a study of these curves that for any particular liquid product yield the octane rating of the product would be higher for the process of our invention (Curve A), and likewise for any particular
20 octane number the yield would be higher. Thus, the curves indicate that for a clear octane rating of 88.2 the yield for the process of our invention would be about 90.0, as compared with only 81.3 per cent for the
25 process carried out without the addition of oxygen. Comparable superiority in yield for our process would be shown for any other desired octane level.

We have conducted additional runs involv-
30 ing hydroisomerization of a charge consisting of a single hydrocarbon in which oxygen was the oxygenic substance employed. Details of the procedure were as follows.

EXAMPLE 6
35 A fluid catalyst consisting of 8.4 per cent molybdenum trioxide deposited on activated alumina impregnated with about 4 per cent

silica was calcined and then reduced in a stream of hydrogen containing about 0.3 mol per cent oxygen at 1050° F. for 4 hours. The reduced catalyst was placed on-stream for hydroisomerization of normal pentane under reaction conditions including a temperature of 875° F., a pressure of 300 pounds per square inch gauge, a liquid hourly space velocity of 1.0 (based on packed catalyst volume), and a hydrogen concentration of about 21,000 standard cubic feet of hydrogen per barrel of liquid pentane. During the reaction the hydrogen stream contained 0.3 mol per cent oxygen. The product of the throughput interval from 1.0 to 3.0 volumes of charge per volume of catalyst, inclusive, was collected. The yield of liquid product for this interval was 86.1 per cent by weight and the product contained 3.2 per cent by weight isopentane.

EXAMPLE 7
The procedure of Example 6 was repeated at a reaction temperature of 925° F. The yield of liquid product for the throughput interval from 1.0 to 3.0, inclusive, was 78.6 per cent by weight, and this product contained 11.1 per cent by weight isopentane.

EXAMPLE 8
The procedure of Example 6 was repeated at a reaction temperature of 950° F. The yield of liquid product for the throughput interval from 1.0 to 3.0, inclusive, was 70.4 per cent by weight, and this product contained 16.0 per cent by weight isopentane.

To show the superiority of our process as carried out in Examples 6 to 8 above, over operating without the use of an oxygenic sub-

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stance, we have conducted comparative runs without the use of oxygen, as described in the following examples.

EXAMPLE 9

5 The treatment of normal pentane according to the procedure of Example 6 was repeated but using a hydrogen stream for both the pre-reduction and on-stream periods which was substantially free of oxygenic substances, and 10 employing a reaction temperature of 721° F. The yield of liquid product of the throughput interval from 1.0 to 3.0, inclusive, was only 51.5 per cent by weight, and this product contained only 0.5 per cent by weight iso-15 pentane.

EXAMPLE 10

The treatment of normal pentane in accordance with Example 9 was repeated at a reaction temperature of 772° F. The yield 20 of liquid product for the throughput interval from 1.0 to 3.0, inclusive, was only 41.1 per cent by weight and contained only 1.8 per cent by weight isopentane.

The results of Examples 6 through 10 illus-25 trate very clearly the superior results of our process, since for all runs conducted in accordance with our process (Examples 6, 7 and 8), both the liquid yields and the percentages of isopentane in the product were 30 much higher than for the process in which no oxygen was introduced to the reaction zone. These examples show also that a considerably higher temperature is employed in our process. Thus, Example 10, which was carried 35 out at a temperature of 772° F., gave a very low liquid yield and indicated that a higher temperature without the addition of oxygen would be undesirable. The lowest temperature run in accordance with our process (Example 40 6) was about 100° F. higher and was not necessarily the highest optimum temperature, since the isopentane yield was not as high as was obtained in the higher temperature runs.

We have also conducted runs which com-45 pare the results of hydroisomerizing methylcyclopentane by our process using oxygen as the oxygenic substance, and by the process in which no oxygen is added. Details of the procedure were as follows.

EXAMPLE 11

50 Methylcyclopentane was subjected to hydroisomerization in the manner described for Example 6, with the exception that the reaction temperature was 974° F. and the 55 hydrogen stream contained about 0.4 mol per cent oxygen both in the prereduction and in the on-stream period. The yield of liquid product for the throughput interval from 1.0 to 3.0, inclusive, was 94.4 per cent by weight, 60 and this product contained 14.9 per cent by volume benzene.

EXAMPLE 12

The hydroisomerization of methylcyclopentane according to the procedure of 65 Example 11 was repeated using a reaction tem-

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perature of 1002° F. The yield of liquid product for the throughput interval from 1.0 to 3.0, inclusive, was 88.2 per cent by weight and this product contained 20.6 per cent by volume benzene. 70

EXAMPLE 13

Methylcyclopentane was treated at a temperature of 848° F. according to the procedure of Example 11 but using a hydrogen stream for both the prereduction and on-stream 75 periods which was substantially free of oxygenic substances. The yield of liquid product for the throughput interval from 1.0 to 3.0, inclusive, was 86.5 per cent by weight, and this product contained 1.9 per cent by volume 80 benzene.

EXAMPLE 14

The treatment of methylcyclopentane according to the procedure of Example 13 was carried out at 896° F. without the addi-85 tion of oxygen. The yield of liquid product for the throughput interval from 1.0 to 3.0, inclusive, was 65.6 per cent by weight, and this product contained 4.2 per cent by volume benzene. 90

The results of the methylcyclopentane isomerizations can be evaluated in terms of benzene production, the benzene being produced by isomerization of methylcyclopentane to cyclohexane which dehydrogenates to 95 benzene. The results clearly show the superiority of our process as carried out in Examples 11 and 12. Examples 11 to 14 show that benzene content of the product increases with temperature while total yield of liquid 100 product decreases with temperature. Examples 12 and 13 produced comparable yields of liquid product although the yield for our process (Example 12) was somewhat higher. The significant fact, however, is that for com-105 parable liquid yields, our process produced more than ten times the amount of benzene produced in the process carried out without the addition of oxygen (Example 13). The results of Example 11 show that when the 110 temperature is somewhat lower than in Example 12, the total production of benzene is somewhat lower although still much higher than produced by either Examples 13 or 14, and the liquid product yield is higher. 115 Example 14 shows that when the temperature is increased above that of Example 13, the yield of benzene is somewhat better, but the total liquid yield is considerably lower, so that obviously no temperature could be selected 120 for the process carried out in the absence of oxygen which would show both the high liquid yields and high conversion to benzene of our process.

We have also conducted experiments which 125 demonstrate the applicability of our process for hydroisomerizing a synthetic mixture of a normal paraffin, a naphthene, and an aromatic compound. The procedure was as follows: 130

EXAMPLE 15

The molybdena-on-alumina fluid catalyst consisting of 8.4 per cent by weight MoO_3 supported on alumina impregnated with about 4 per cent silica was precalcined at 1100° F. in a stream of air and then prereduced at 1050° F. in a stream of hydrogen containing 0.28 mol per cent oxygen. The catalyst was then fluished with pure nitrogen, cooled to 900° F., and pressured to 300 pounds per square inch gauge with hydrogen containing 0.28 mol per cent oxygen. This catalyst was then placed on-stream for hydroisomerizing a mixture consisting of 39.1 per cent by weight pure-grade normal pentane, 48.7 per cent by weight pure-grade cyclohexane, and 12.2 per cent by weight chemically pure benzene. Reaction conditions included temperature of 899° F., space velocity of 1.0 volume of liquid charge per volume of packed catalyst per hour, pressure of 300 pounds per square inch gauge, and hydrogen concentration of 21,000 standard cubic feet of hydrogen per barrel of liquid charge. The hydrogen stream contained oxygen in the amount of 0.28 mol per cent. The product of the throughput interval from 1.0 to 3.0, inclusive, was analyzed and the results in terms of the yield and characteristics of this product are given in Table II below.

EXAMPLES 16—23

The procedure of Example 15 was repeated under the same conditions employed in Example 15 but with variations in temperature and mol per cent of oxygen in the hydrogen stream as follows:

Example No.	Temperature, ° F.	Mol % O_2 in H_2 Stream
16	900	0.23
17	924	0.23
18	926	0.28
19	950	0.28
20	970	0.23
21	984	0.28
22	985	0.28
23	1004	0.28

In each of the above runs the catalyst was prereduced with a hydrogen stream containing the same amount of oxygen as used in the on-stream period. The results for Examples 16 to 23 in terms of yield and characteristics of the product of throughput interval from 1.0 to 3.0, inclusive, are listed in Table II below.

We have also conducted hydroisomerization runs according to our procedure in which steam is employed as the added oxygenic substances. The details of procedure were as follows:

EXAMPLE 24

The hydroisomerization of the normal pentane, cyclohexane, benzene mixture of Example 15 was repeated using the catalyst of Example 15, precalcining and prereducing the catalyst in the manner described with the exception that the hydrogen stream for pre-reduction contained steam instead of oxygen in the amount of 17.1 mol per cent steam. Reaction conditions included temperature 960° F., space velocity 1.0 volume of liquid charge per volume of packed catalyst per hour, pressure 300 pounds per square inch, hydrogen concentration 21,000 standard cubic feet of hydrogen per barrel of liquid charge, and the hydrogen recycle stream contained 0.8 mol per cent steam. The results in terms of the yield and characteristics of the product of throughput interval from 1.0 to 3.0 inclusive volumes of liquid per volume of packed catalyst are listed in Table II below.

EXAMPLES 25—26

The procedure of Example 24 was repeated, but using hydrogen for prereduction which had the same steam content as the on-stream hydrogen, i.e., 0.8 mol per cent, and using temperatures of 975° F. and 985° F., respectively. The yields and characteristics of the products for the throughput intervals from 1.0 to 3.0 inclusive are given in Table II below.

The superiority of our procedure for hydro-isomerizing the n-pentane, cyclohexane, benzene mixture is shown by comparative runs on this mixture without the addition of an oxygenic substance to the reaction zone. Details of procedure were as follows:

EXAMPLE 27

The molybdena-alumina catalyst of Example 15 was precalcined and then prereduced in a stream of pure hydrogen and placed on-stream for the treatment of the n-pentane, cyclohexane, benzene mixture. The hydrogen stream was substantially free of oxygenic substances and no oxygenic substances were added to the reaction zone after the start of the process. Reaction conditions included temperature 851° F., space velocity 1.0 volume of liquid charge per volume of packed catalyst per hour, pressure 300 pounds per square inch gauge, hydrogen concentration 21,000 standard cubic feet of hydrogen per barrel of liquid charge. The yield and characteristics of the product for the throughput interval from 1.0 to 3.0 volumes of liquid charge per volume of

packed catalyst inclusive are listed in Table II below.

EXAMPLES 28—32

The procedure of Example 27 was repeated with variations in the reaction temperature as follows:

Example No.	Temperature, °F.
28	869
29	884
30	897
31	897
32	903

The yields and characteristics of the products for throughput intervals from 1.0 to 3.0 volumes of liquid charge per volume of packed catalyst inclusive are listed in Table II below.

TABLE II

Yields of Various Products: % by Wt.

Example No.	Mol % Oxygenic substance in Hydrogen Stream	Run Temp. °F.	Liquid Product % by Wt. of Charge Mixture	C₁ to C₄	i—C₅	n—C₆	Benzene	Cyclohexane and saturated C₆ isomers	Composition of cyclohexane and saturated C₆ isomers: 100 Vol. %			Total yield of C₆: % by wt.	Total yield of C₆: % by wt.
									Hexane	Methyl-cyclo pentane	Cyclo-hexane		
Charge	—		—			39.1	12.2	48.7				39.1	60.9
15	0.28 (oxygen)	899	95.0	4.5	2.3	34.6	29.8	29.2	1.9	40.8	57.3	36.9	58.1
16	0.23	900	95.7	0.8	1.5	33.2	26.8	34.2				34.7	61.0
17	0.23 ,,	924	—	—	—	—	31.7	28.6				—	60.3
18	0.28 ,,	926	96.4	3.8	3.3	33.6	28.6	30.9	3.2	46.3	50.5	36.9	59.5
19	0.28 ,,	950	92.9	5.1	5.0	29.9	32.5	25.5	4.8	48.5	46.7	34.9	58.0
20	0.23 ,,	970	90.8	0.2	7.6	26.9	39.5	16.8	8.0	51.4	40.6	34.5	56.3
21	0.28 ,,	984	95.9	4.7	8.8	28.9	38.9	19.3	9.4	55.0	35.6	37.7	58.2
22	0.28 ,,	985	92.9	—	8.2	28.1	40.7	15.9	10.2	61.1	28.7	36.3	56.6
23	0.28 ,,	1004	85.3	5.7	9.1	22.9	38.9	14.4	13.3	49.6	37.1	32.0	53.3
24	0.8 (steam)	960	93.7	5.3	5.7	30.5	29.4	28.1				36.2	57.5
25	0.8 ,,	975	91.0	4.7	7.1	28.4	33.6	21.9				35.5	55.5
26	0.8 ,,	985	91.5	7.4	8.2	27.2	37.4	18.7				35.4	56.1
27	<0.01	851	87.5	8.0	2.0	30.7	35.2	19.6	8.7	20.6	70.7	32.7	54.8
28	<0.01	869	85.8	18.2	1.8	30.6	38.3	15.1	6.1	21.2	72.8	32.4	53.4
29	<0.01	884	78.8	23.6	2.3	26.6	38.8	11.1				28.9	49.9
30	<0.01	897	72.5	30.2	3.0	19.8	43.5	6.2				22.8	49.7
31	<0.01	897	71.2	27.9	2.7	21.5	37.9	9.1	13.9	16.7	69.4	24.2	47.0
32	<0.01	903	60.4	38.0	3.3	14.9	39.5	2.7	32.6	20.9	46.5	18.2	42.2

The results listed in Table II show the great improvements afforded by our procedure of hydroisomerizing while maintaining the molybdenum catalyst in the proper state of oxidation by the introduction of an oxygenic substance to the reaction zone. The superior results of our procedure as compared with treating the same charge stock without the addition of an oxygenic substance were obtained with either steam or oxygen as the oxygenic substance. Thus the yields of total liquid product were greater for all runs in accordance with our process, with the exception of the yield for the highest temperature run by our process (Example 23) as compared with the lowest temperature run by the procedure in which no oxygen was added (Example 27). Even in these latter two runs the total liquid product yields were substantially equal while the yield of isopentane was much greater for our process and the yield of benzene was somewhat greater.

The significance of these data can be most clearly understood by a study of the data in graphic form as presented in Figures 2 and 3 of the drawing. Thus, referring to Figure 2, it is seen that our process, as represented by Curve A, gives sustained high liquid product yields up to a temperature above 1000° F. while the liquid yield for the process in which no oxygenic substance was used drops sharply at a temperature of about 870° F. as shown by Curve B. Thus, if temperatures sufficiently high to give the desired high conversions to branched chain paraffins are employed without the addition of oxygenic substances, cracking is excessive and liquid yields decrease greatly.

Figure 3 gives a clear comparison of the relationship between yield of isopentane and recovery of total pentanes in our process and in the process in which no oxygen is used. Thus, Curve A of Figure 3 shows a sustained high yield of total pentanes with increase in isopentane yield for our process, while Curve B shows a sharp drop in total pentane yield

as the yield of isopentane increases.

It is quite clear from the results shown in Table II and in Figures 2 and 3 that our procedure of hydroisomerizing under properly controlled oxidation-reduction conditions in the reaction zone is a great improvement over operating without proper control of the oxidation-reduction conditions when treating a normal-paraffin, naphthene, aromatic mixture. As Table II and Figures 2 and 3 show, our superior results were obtained with either oxygen or steam employed as the oxygenic substance although a higher mol concentration of steam was used.

We have conducted additional runs which show the effect on hydroisomerization results of the concentration of the oxygenic substance in the conversion zone. Details of procedure were as follows:

EXAMPLES 33 AND 34

The n-pentane, cyclohexane, benzene mixture described in Example 15 was subjected to hydroisomerization under conditions including temperature of 980° F., pressure of 300 pounds per square inch, space velocity of 1.0 volume of liquid charge per volume of packed catalyst per hour, and hydrogen concentration of 21,000 standard cubic feet of hydrogen per barrel of liquid charge. Run 33 was made using the molybdena-alumina fluid catalyst consisting of 8.4 per cent MoO_3 on alumina impregnated with about 4 per cent silica. Run 34 was made with the molybdena-alumina fluid catalyst consisting of 10.8 per cent MoO_3 on alumina coprecipitated with 5 to 6 per cent silica. The concentration of oxygenic substance in the hydrogen used for prereduction and the hydrogen used in the onstream period was different for each run. The concentrations used are listed in Table III below. The runs used steam as the oxygenic substance. Table III also lists the yields of products obtained during the throughput interval of from 1.0 to 3.0 volumes of liquid charge per volume of packed catalyst inclusive.

The data of Table III show that the yields of benzene and isopentane for Example 34 were very good.

As stated previously, the present process is particularly effective, when employed for the treatment of hydrocarbons boiling in the naphtha and gasoline boiling range; i.e. hydrocarbons which in admixture produce a mixture boiling within the range of about 32° to about 550° F. Thus, the hydrocarbons can be referred to as naphtha hydrocarbons.

What we claim is: —

1. A hydroisomerization process for the treatment of hydrocarbons which comprises contacting the hydrocarbon and hydrogen in proportions of at least 500 cubic feet of hydrogen per barrel of said hydrocarbon with a catalyst comprising a molybdenum oxide at a pressure above 50 pounds per square inch and at a temperature of at least 850° F. and including in the charge to the reaction zone an amount of oxygen, steam or carbon dioxide supplying 0.0023 to 0.03 mol of oxygen per mol of hydrogen.

2. The process according to claim 1, in which the hydrocarbon is a naphtha.

3. A process according to claim 1 or 2, in which the reaction is effected at a temperature between 850° and 1100° F.

4. A process according to claim 2 or 3, applied to a charge comprising a straight-run naphtha and hydrogen in proportions of 1,000 to 20,000 cubic feet of hydrogen per barrel of said naphtha.

5. A process according to any of the preceding claims, in which the molybdenum oxide is supported on an alumina base.

6. A process according to any preceding claim, carried out at least 50° F. above the temperature at which an equal liquid product yield would be obtained when treating the hydrocarbon under the same conditions but omitting the oxygen, steam or CO_2 from the charge to the reaction zone.

7. A process according to any preceding claim, in which a naphtha straight-chain paraffin hydrocarbon is treated.

8. A process according to claim 7, in which the naphtha straight-chain paraffin hydrocarbon is normal pentane.

9. A process according to any preceding claim, which comprises reducing a regenerated molybdenum oxide catalyst with hydrogen containing an amount of oxygen, steam or carbon dioxide supplying 0.0023 to 0.03 mol of oxygen per mol of hydrogen, and then contacting the resulting reduced catalyst in the reaction zone with the charge comprising a naphtha hydrocarbon and hydrogen in the aforesaid proportions and in the aforesaid ranges of pressure and temperature, and including in the charge to the reaction zone oxygen, steam or carbon dioxide in the aforesaid amount.

Table III

Example No.	Mol % steam equivalent in on-stream hydrogen	Mol % steam equivalent in hydrogen used for prereduction	Run Temp. °F.	Yield of Various Products: % by wt.					Total yield of C_5: % by wt.	Total yield of C_6: % by wt.	Total yield of liquid products % by wt.
				C_1 to C_4	i—C_5	n—C_5	Benzene	Cyclohexane and saturated C_6 isomers			
33	1.60	1.60	891	2.7	8.9	27.6	35.4	20.3	36.5	55.7	92.2
34	1.0	1.0	980	10.2	11.3	24.9	32.8	21.6	36.2	54.4	90.6

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10. The hydroisomerization processes for treating hydrocarbons, as herein particularly described and ascertained in any of Examples 1 to 3, 6 to 8, 11, 12, 15 to 26, 33 and 34, or its obvious equivalents.

11. The products of the treatment of hydrocarbons by a hydroisomerization process as claimed in any preceding claim.

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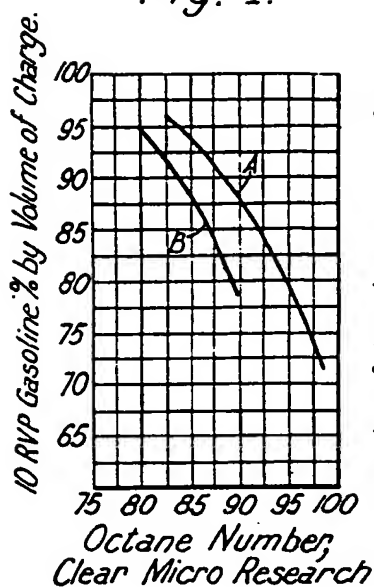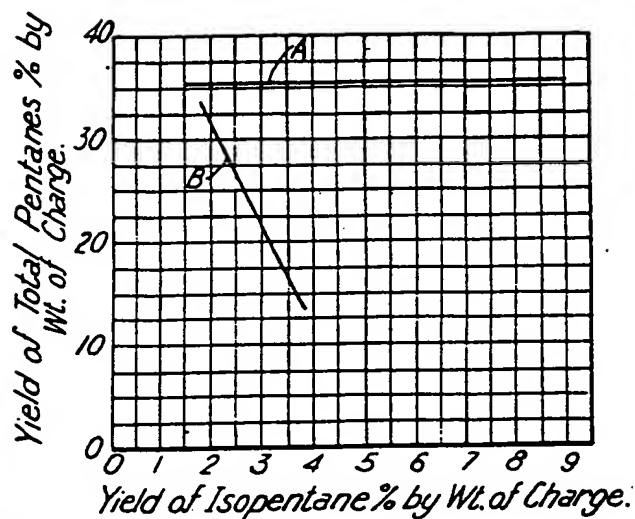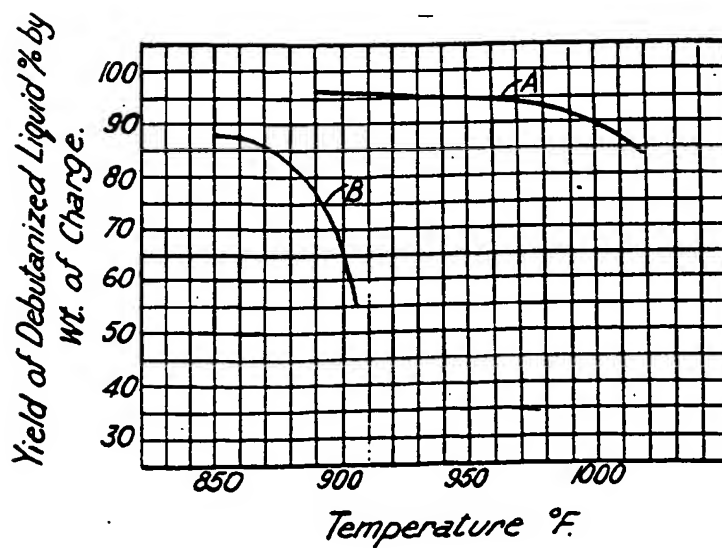1 SHEET   This drawing is a reproduction of
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Fig. 1.

Fig. 3.

Fig. 2.

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